

CHARACTERIZATION OF MAGNETITE WITHIN CARBONATE IN ALH84001. David Blake¹, Allan Treiman², Sherry Cady³, Chris Nelson⁴ and Kannan Krishnan⁴, ¹Exobiology Branch, MS 239-4, NASA Ames Research Center, Moffett Field, CA. ²Lunar & Planetary Institute, 3600 Bay Area Blvd. Houston, TX. ³SETI Institute, MS 239-4, Moffett Field, CA 94035. ⁴National Center for Electron Microscopy, Lawrence Berkeley Laboratory, Berkeley, CA.

Introduction. Nanocrystalline iron oxide, identified as magnetite, is found within iron-rich bands associated with carbonate in ALH84001 in all modes of its occurrence, including “carbonate pancakes”, “carbonate globules”, “framework carbonate globules” and “vein carbonates”. McKay et al¹ proposed that the magnetite was biogenic in origin, because individual crystals were the proper size to be magnetic single domains, were defect-free, and coexisted with other metastable phases in apparent disequilibrium. Bradley² reported screw dislocations in acicular magnetite crystals and cited this as evidence of its origin by vapor-growth. Here, we present evidence that equant magnetite crystals present within and near iron rich bands in the carbonate are the product of inorganic solution-precipitation processes.

Samples and methods. 3 mm washer grids of Cu were epoxied onto thin section ALH84001,145 (made with superglue). The washers and attached thin section material were detached from the section by soaking in acetone. A washer containing a framework carbonate globule, shown in figure 7 of Treiman³ was chosen for study. This section was characterized by optical petrography and SEM / EMP prior to argon ion thinning and observation in a Philips 200 KeV Field Emission Electron Microscope. A Gatan Imaging Filter was used to obtain chemical bonding data, and a Link Atmospheric Thin Window Energy-Dispersive X-ray (EDS) detector was used to obtain elemental compositions.

Mineralogical identity of the iron oxide. We used Electron Energy Loss Spectroscopy (EELS) to characterize the magnetite in the iron-rich layers of the carbonate globule. EELS energy scans over the K absorption edges of Fe and O were obtained for a total of 7 individual magnetite grains, as well as for magnetite, hematite and maghemite standards. Iron oxide grains from the carbonate globule had oxygen K absorption edge features identical to the magnetite standard, but different from hematite and maghemite standards (Fig. 1). This is the first definitive identification of the iron oxide crystals as magnetite. Electron diffraction methods cannot readily distinguish magnetite from maghemite, another spinel structure iron oxide mineral, with significantly different petrogenetic implications. Magnetite crystals within the iron rich band are commonly equant, 20-60 nm in size, and show few defects in high resolution structure images (Fig. 2). Many of the crystals are faceted.

Inclusions within ankeritic carbonate. In the ankeritic carbonate adjacent to the innermost magnetite-rich layer are numerous holes (void spaces) and holes containing mineral inclusions (fig. 3). The inclusion

minerals are magnetite, based on TEM structure images and qualitative EDS spectra. High resolution images of the crystals show that they are defect-free, and some are in the proper orientation to show epitaxial or near-epitaxial orientation with the host carbonate. These holes and magnetite grains may have formed from inclusions of “mineralizing” fluid trapped in the ankerite.

Minor elements within adjacent phases. EDS microanalyses of magnetites in the iron-rich bands and inclusions in the ankerite, and host orthopyroxene all show similar inventories of minor elements, including Ni, Mn and Cr. In some cases, magnetite grains are associated with minor quantities of S, Si and Mg.

Discussion. We confirm many of the previously reported findings of McKay and others, including the identification of the nanocrystalline iron oxide as magnetite, its “single magnetic domain” size range, the structural perfection of individual crystals and the presence of facets on some crystals. We also find numerous holes and magnetite-containing inclusions in the ankeritic carbonate near the iron-rich bands. Some of these crystals are in epitaxial orientation with the surrounding ankeritic carbonate. Epitaxial relationships strongly suggest that one phase grew directly on the other since it would be difficult to understand how such a precise orientation could occur at random, or how, once formed, a crystal could become epitaxially oriented with respect to the calcite. Less compelling, but also suggestive of an inorganic origin, is the similar minor element inventories of the magnetite, ankeritic carbonate and pyroxene.

Analogs of ALH84001 magnetite. We are not aware of any satisfactory terrestrial analog for the magnetite in ALH84001, save the biogenic forms proposed by McKay et al.¹ However, there are hints from laboratory experiments that comparable magnetite-carbonate textures can form inorganically. Holser and Schnee⁴ were able to grow equant, euhedral (faceted) magnetite crystals from aqueous solution onto calcite at temperatures from 320° C to 150° C. The smallest magnetite crystals visible in their figures are ~20µm diameter, and the crystals appear epitaxially oriented with the host calcite. Holser and Schnee’s results are not directly applicable to the magnetites in ALH84001, but do suggest a possible mechanism for inorganic formation of magnetite-carbonate intergrowths from “low-temperature” aqueous solutions.

References: [1] McKay et al. *Science* **274**, 2123 (1996). [2] Bradley et al., *Geochim. Cosmochim. Acta* **60**, 5149 (1997). [3] Treiman A.H. *Meteoritics* **30**, 294 (1995). [4] Holser and Schnee, *GSA Bull* **72**, 369 (1961).

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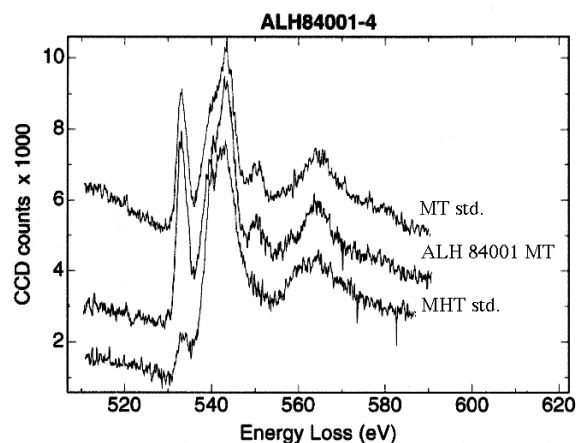


Figure 1. Electron energy-loss spectra of the oxygen K edge for magnetite (MT), maghemite (MHT) and ALH84001 magnetite. The edge features at 535 and 550 eV are prominent in both the ALH84001 and MT standard, but weak to absent in the MHT standard.

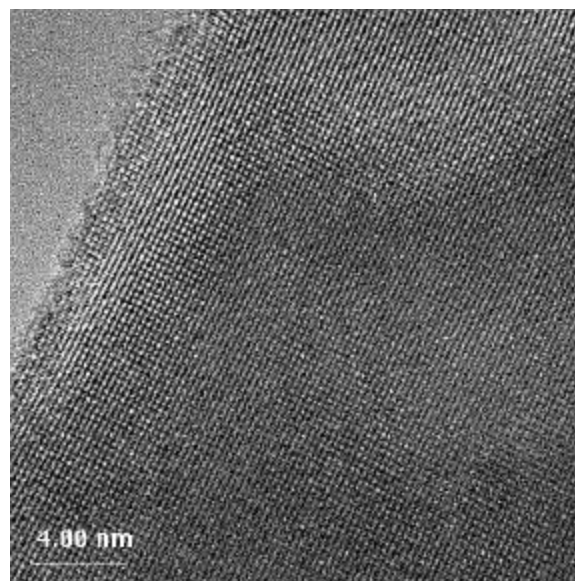


Figure 2. High resolution image of magnetite grain in iron-rich layer of carbonate globule. Note the absence of defects in the structure and the existence of a faceted edge (i.e., edge parallel with crystallographic direction).

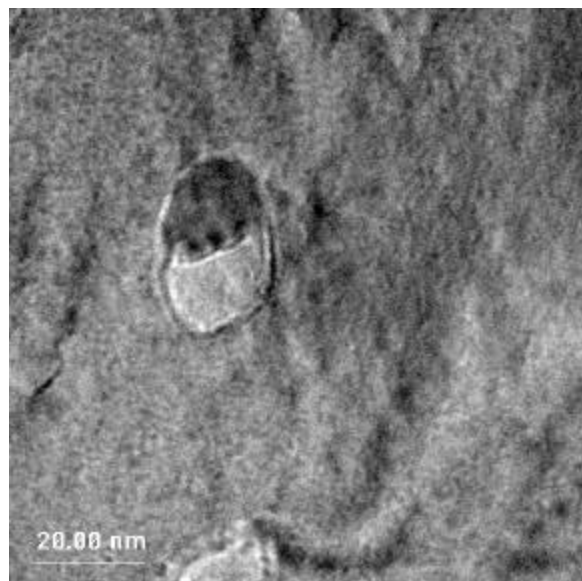


Figure 3. Low magnification image of a hole containing a mineral inclusion within the ankerite. Many such holes exist within the ankerite in close proximity to the iron-rich zone. Holes range from 10's to 100's of nanometers.

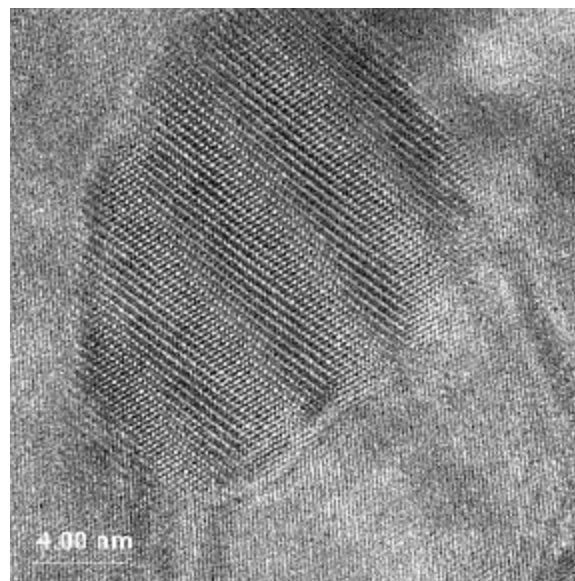


Figure 4. Structure image of crystal within inclusion shown in figure 3. The crystal was identified as magnetite by measurement of lattice fringe spacings and by qualitative EDS analysis. The magnetite is in epitaxial orientation with the host ankerite.